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NATURE OF THE GLASS IN PORTLAND CEMENT CLINKER

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ABSTRACT

New microscopical methods resulting in more accurate differentiation of the minor constituents of portland cement clinker are described which involve the etching of polished surfaces of the clinker grains by strong alkaline solutions. By the new technique it is possible to identify interstitial glass high in iron which heretofore has been confused in microscopical analysis with $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. The results of microscopical analysis, using the new etching technique, are compared with results of an older microscopical method and with those of a heat-of-solution method.

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I. INTRODUCTION

In a recent paper [1]¹ a method was outlined for determining quantitatively the constituents in portland cement clinker by the microscopical analysis of polished surfaces of clinker after etching with suitable reagents. The constituents $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, "light interstitial" material, "crystalline dark interstitial" material, "glassy dark interstitial" material, free CaO , and free MgO were differentiated by using as etching reagents water followed by a 1 percent alcoholic solution of HNO_3 . The quantitative analyses were made with a recording micrometer stage attached to the microscope. The volume proportions thus found were calculated to weight percentages by assigning density values to the constituents. Twenty-six samples of commercial portland cement clinker analyzed by the method just described were also analyzed chemically and the results calculated to compound composition by the Bogue method [2]. For 14 of these samples the glass content was determined by an independent method involving the determination of the heat of solution [3].

A comparison of the results of the different methods showed that the amount of glass found by the heat-of-solution method was greater in every case than was found by the microscopical method and that the amount of "light interstitial" material determined microscopically was greater than the $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ calculated from chemical analyses for samples with $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ ratios less than 2.00. Indeed, for several samples the microscopically determined "light interstitial"

¹ Figures in brackets indicate the literature references at the end of this paper.

material equalled or exceeded the sum of the calculated $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. The observation was made in the former paper that attempts to differentiate the "light interstitial" material into two phases (for instance, the compound $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ and a highly refractive glass) by the use of etching reagents or illumination methods had thus far been unsuccessful.

Since the publication of that paper, the search for an explanation of the discrepancies mentioned has been renewed. The present paper is a record of some of the methods tried and a description of the method found successful, together with corrected results of the quantitative microscopical analysis, using the new method.

II. METHODS AND RESULTS

1. QUALITATIVE ANALYSES

As material for investigation three samples were selected from the 26 samples of commercial clinker previously studied. These samples, numbered originally 11, 12, and 16, showed the greatest differences between glass as determined microscopically and as determined by the heat-of-solution method. For the same samples microscopically determined, "light interstitial" material was also considerably greater than the calculated $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. The pertinent data, in weight percentages, are given in table 1.

TABLE 1.—*Content of interstitial materials in clinker samples*

Sample No. ¹	Light interstitial		Glass	
	$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ ²	Microscopic	Microscopic	Lerch method ³
	Percent	Percent	Percent	Percent
11	15	23	4	12
12	13	20	3	10
16	12	23	2	11

¹ From table 2 [1].

² Calculated by the Bogue method.

³ The heat-of-solution method [3].

Specimens of all three clinker samples were first investigated by examining the powdered specimens in transmitted light with the petrographic microscope. The powders were immersed in a liquid of refractive index 1.74 so that all clinker constituents except $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ and iron-bearing glass would have indices of refraction less than that of the immersion liquid. Using an arc lamp as light source and an oil-immersion objective, the grains with index higher than 1.74 were carefully tested for the presence or absence of material having double refraction. Practically all grains so examined contained prismatic birefringent crystals often pleochroic with a greenish-amber color and having indices of refraction markedly higher than that of the immersion medium. In some grains these crystals were intermingled, forming such a mat that no isotropic material could be seen, whereas in others what apparently was a greenish isotropic material formed a matrix for a few of the tiny crystals. The presence of an isotropic interstitial material with high index of refraction could not, however, be conclusively demonstrated by this method.

A study was then made of the effect of various etching reagents on polished surfaces examined in reflected light. Specimens of the same three clinker samples were used. A number of solutions in varying concentrations and for various etching periods failed to give any clear-cut differentiation of the light interstitial material.²

Neither oxalic acid nor hydrofluoric acid, recommended by Tavasci [4] to distinguish "celite a" from "celite b," was found to be of help in this problem. Another reagent mentioned by Tavasci for etching $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, a mixture of 4 parts by volume of 10 percent NaOH and 1 part of 10 percent Na_2HPO_4 , when used under the specified conditions of 50°C for 1 minute, etched all the interstitial material indiscriminately. At room temperature, however, portions of the interstitial material were etched very slightly by this reagent, whereas other portions were etched more deeply. The more deeply etched areas included those etched by water and by the alcoholic solution of HNO_3 as well as much interstitial material left unetched by these reagents. Attention was, therefore, turned to strongly alkaline solutions. Both NaOH and KOH were satisfactory under proper conditions, but KOH produced stronger etching of the dark interstitial material and gave better contrast of the etched with the unetched material. A 10 percent aqueous solution in contact with the polished specimen for 15 seconds at 29° to 30°C gave the best results. The marked increase in the dark interstitial material shown by the KOH etch over that shown by the water and HNO_3 etches in clinkers with low $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ ratios can be seen by a comparison of figure 1 with figure 2. Much interstitial material apparently unetched in figure 1 is shown deeply etched in figure 2. In a quantitative microscopical analysis the material shown as unetched by water and HNO_3 in figure 1 would be included under light interstitial material, whereas much of the same area would be included in dark interstitial material as etched by KOH (fig. 2).

Figures 3 and 4 are of a polished area from another piece in the same clinker batch as represented in figures 1 and 2. The mottled effect seen in the dark interstitial area in figure 2, and more noticeably in figure 4, indicates that such areas are not composed of a single homogeneous phase. Examination of similar areas in polished thin sections with transmitted light shows the presence of an isotropic material with green color and a high refractive index. Such optical properties are characteristic of a glass containing a considerable amount of iron. This material is the matrix for tiny, amber, needle-like crystals, with high index of refraction and moderately high birefringence, having the appearance of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. Areas like the unetched interstitial areas in figures 2 and 4 contain much larger crystals of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ without accompanying glass. Such areas were found very close to the surface of small clinker grains less than 6 mm in diameter. It is impossible to say whether or not a concentration of certain constituents near the surface caused by a volatilization of alkalis or by a migration of iron oxide was responsible for this condition. Larger clinker grains from the same batch contain interstitial material like that shown in figures 5 and 6, the glass apparently forming a matrix for prismatic crystals of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. Figures 7 and 8 illustrate the relations of interstitial material in clinker

² It was observed incidentally that a 5-percent solution of NH_4Cl in water, when applied for about 3 seconds at room temperature, brought out more clearly than other reagents the internal structure of crystals of $2\text{CaO} \cdot \text{SiO}_2$ and $3\text{CaO} \cdot \text{SiO}_2$, especially zonal growths and twinning bands.

sample 11 with an $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ ratio of 1.12. In this clinker sample the ratio of $4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$ to glass is obviously greater than in sample 16, probably because of the lower $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ ratio in the former.

The nature and etching behavior of the interstitial constituents are confirmed by a study of polished sections of mixtures composed only of CaO , Al_2O_3 , Fe_2O_3 , and SiO_2 , heated and quenched under known conditions. Samples of one such mixture having the composition CaO 63.7 percent, SiO_2 24.5 percent, Al_2O_3 5.9 percent, and Fe_2O_3 5.9 percent, with the calculated compound composition (by the Bogue method) of $3\text{CaO}.\text{SiO}_2$ 25 percent, $2\text{CaO}.\text{SiO}_2$ 51 percent, $3\text{CaO}.\text{Al}_2\text{O}_3$ 6 percent, and $4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$ 18 percent, were quenched from the temperatures $1,500^\circ$, $1,345^\circ$, $1,340^\circ$ and $1,330^\circ$ C. In spite of care, preparations entirely free of quench growths were not obtained. A favorable area in the $1,500^\circ$ C preparation showing few quench growths is seen in figure 9 after etching with H_2O for 3 seconds followed by a 0.25 percent alcoholic solution of HNO_3 for 3 seconds. The interstitial material appears highly reflecting and homogeneous. After treatment with 10 percent KOH solution for 15 seconds at 30° C, the interstitial material is etched and darkened (fig. 10) without showing evidence of differentiation. The $1,345^\circ$ C preparation should, according to the equilibrium diagram of this system [5], contain crystals of $4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$ and glass in the interstitial material. As seen in figure 11, the interstitial material shows a slight differentiation into light and dark areas after etching with water and nitric acid and a much more pronounced differentiation after etching with the 10 percent KOH solution (fig. 12). In the $1,340^\circ$ C preparation differentiation with the water and nitric acid etches (figs. 13 and 14) is still more pronounced than in the $1,345^\circ$ C preparation (fig. 11) and the quantity of light interstitial material ($4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$) has increased at the expense of the dark interstitial material (glass). In the preparation which was quenched at $1,330^\circ$ C, a temperature below the invariant temperature ($1,338^\circ$ C) in this portion of the system $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3$ [5], the interstitial constituents, crystalline $4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$ and crystalline $3\text{CaO}.\text{Al}_2\text{O}_3$, are readily differentiated with H_2O and HNO_3 (fig. 15). Further treatment with KOH etches the $3\text{CaO}.\text{Al}_2\text{O}_3$ more deeply, but does not increase the apparent amount of the etched interstitial material (fig. 16).

Parker and Nurse [6] have deduced from indirect evidence that the nitric acid solution etches glasses in portland cement clinker relatively low in iron but not those high in iron. The preceding group of experiments confirms this deduction, because the amount of Fe_2O_3 in the glass is decreased as the temperature of heat treatment is lowered.

It is not safe, however, to draw conclusions concerning the iron content of glasses in commercial clinkers from such laboratory experiments. Figures 2 and 6 are photomicrographs of different clinker pieces from the same commercial sample. It is apparent that the structure of the interstitial matter and the relative amounts of glass present are quite different and, therefore, it is reasonable to assume that the iron content of the glass in the two pieces is different. Such differences in individual pieces may be caused not only by variations in the composition of the batch but by the rates at which the clinker pebbles pass from the hot zone of the rotary kiln to the exit end.

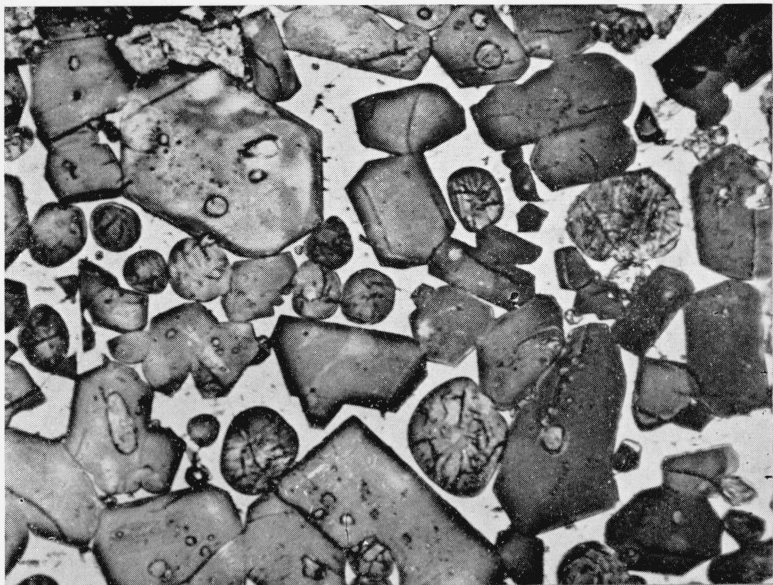


FIGURE 1.—Clinker sample 16 ($\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3=1.34$) after etching with water for 2 seconds followed by a 1-percent alcoholic solution of HNO_3 for 2 seconds.

Lack of differentiation of interstitial material is shown. Reflected light. Magnification, $\times 500$.

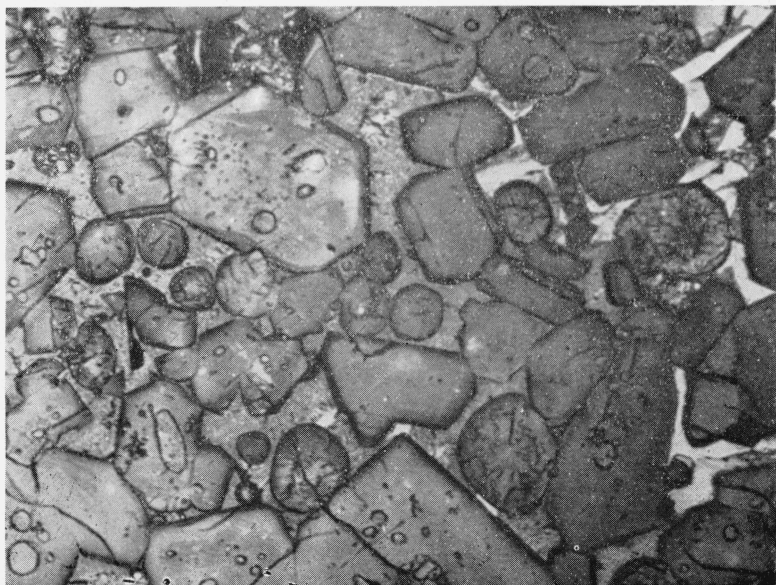


FIGURE 2.—Same field as figure 1 after the same etching treatment and an additional etching with 10 percent KOH for 15 seconds at 29° C.

Marked differentiation of interstitial material is shown. Reflected light. Magnification, $\times 500$.

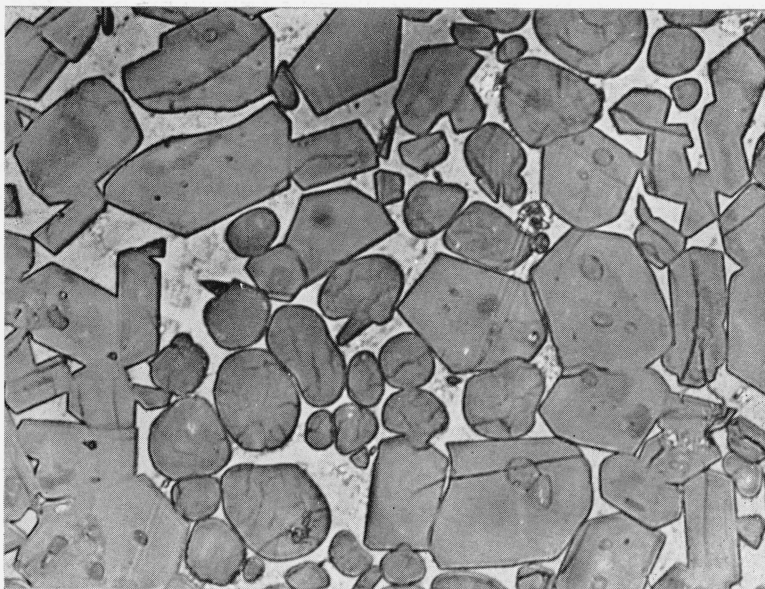


FIGURE 3.—Clinker sample 16 (a different field from fig. 1) after etching with water and a 1-percent alcoholic solution of HNO_3 .

Reflected light. Magnification, $\times 500$.

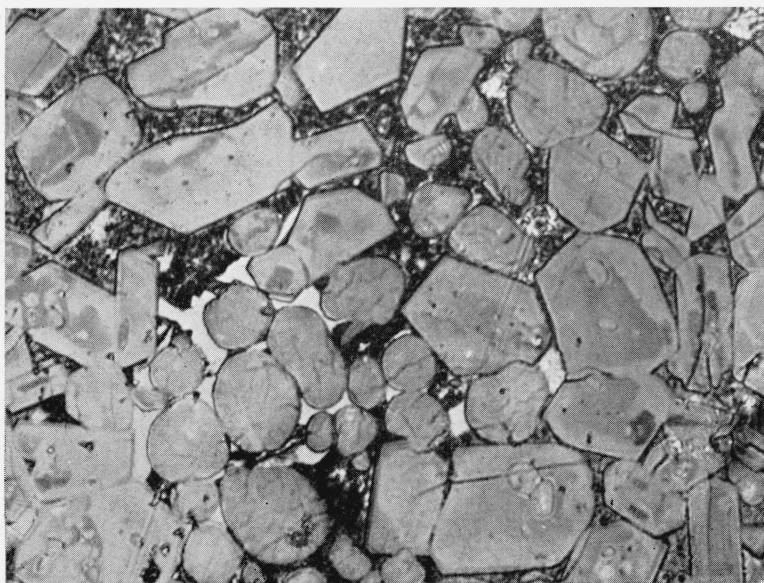


FIGURE 4.—Same field as figure 3 after the same etching treatment and an additional etching with 10 percent KOH.

Showing marked differentiation of interstitial material with intimate mixture of glass and small C_4AF crystals in deeply etched interstitial areas. Magnification, $\times 500$.



FIGURE 5.—Clinker sample 16 (a different field from figures 1 and 3) after etching with water and a 1-percent alcoholic solution of HNO_3 .

Slight differentiation of interstitial material is shown. Reflected light. Magnification, $\times 500$.

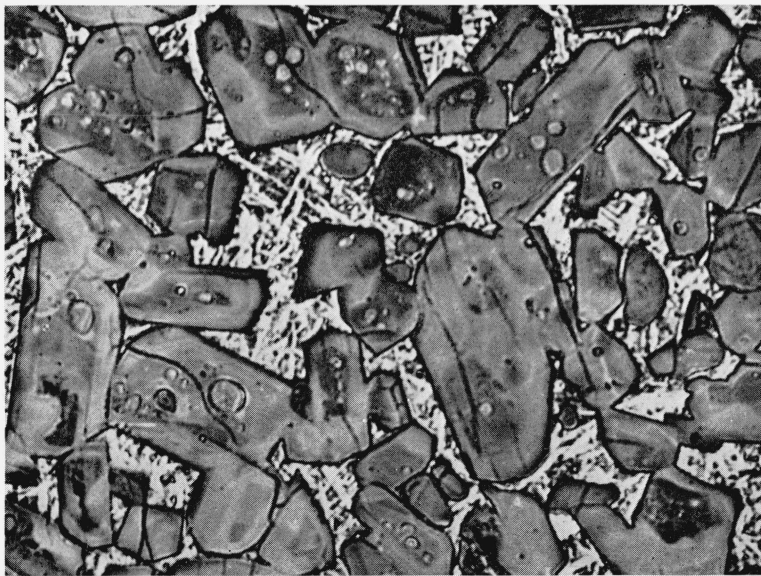


FIGURE 6.—Same field as figure 5 after the same etching treatment and an additional etching with 10 percent KOH .

Marked differentiation of interstitial material into prismatic C_4AF crystals and matrix glass is shown. Magnification, $\times 500$.

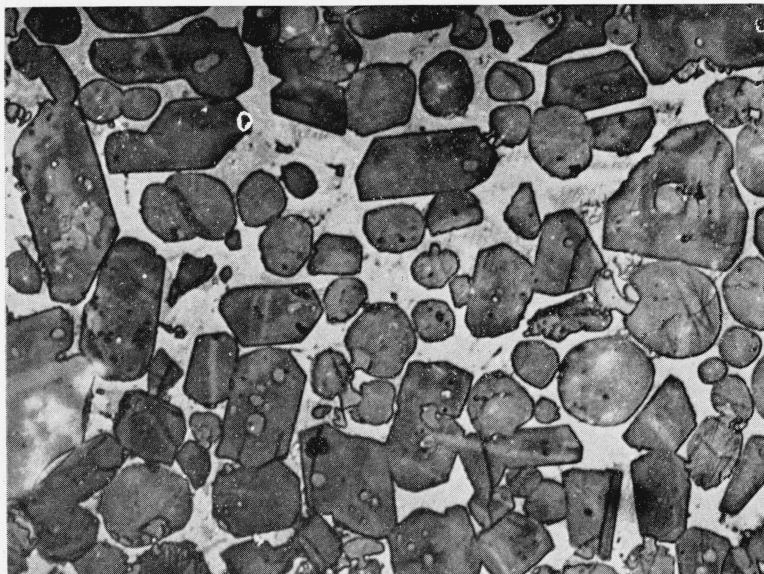


FIGURE 7.—Clinker sample 11 ($\text{Al}_2\text{O}_3=1.12$) after etching with water followed by 1-percent alcoholic solution of HNO_3 .

Very slight differentiation of interstitial material is shown. Reflected light. Magnification, $\times 500$.



FIGURE 8.—Same field as figure 7 after the same etching treatment and an additional etching treatment with 10 percent KOH.

Relatively larger amounts of C_4AF and smaller amounts of glass than in clinker sample 16 are shown. Reflected light. Magnification, $\times 500$.

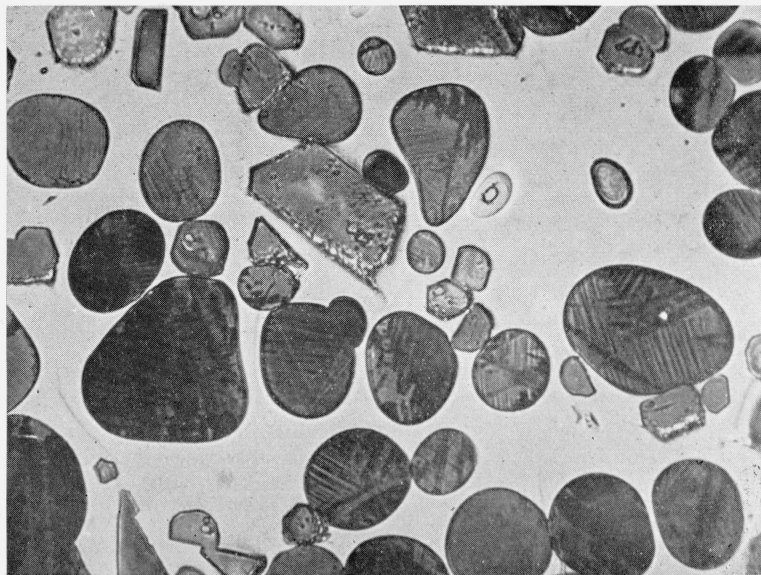


FIGURE 9.—Laboratory-prepared low-heat clinker quenched after heating at $1,500^{\circ}\text{C}$.

Etched with water for 2 seconds followed by 1-percent alcoholic solution of HNO_3 for 2 seconds. Highly reflecting, undifferentiated character of interstitial material is shown. Reflected light. Magnification, $\times 730$.

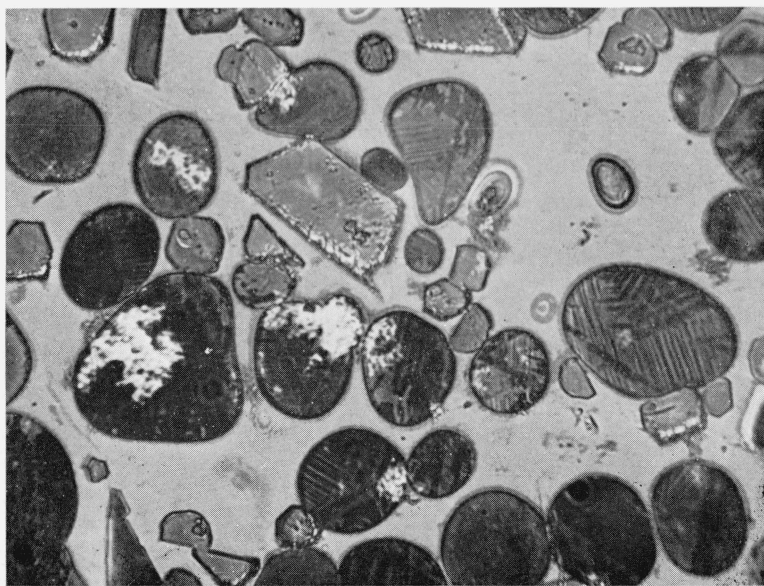


FIGURE 10.—Same field as figure 9 after the same etching treatment and an additional etching with 10 percent KOH for 15 seconds at 29°C .

The appearance of quench-growth halos around C_3S grains and a general decrease in reflectivity of the interstitial material are shown. Reflected light. Magnification $\times 730$.

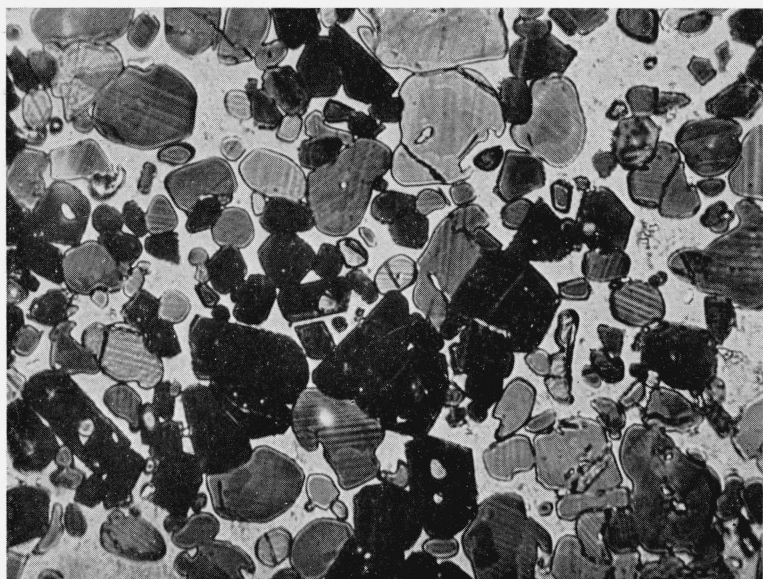


FIGURE 11.—*Laboratory-prepared tow-heat clinker quenched after heating at 1,345° C. Etched with water and 1-percent alcoholic solution of HNO_3 . Very slight differentiation of interstitial material is shown. Reflected light. Magnification, $\times 730$.*

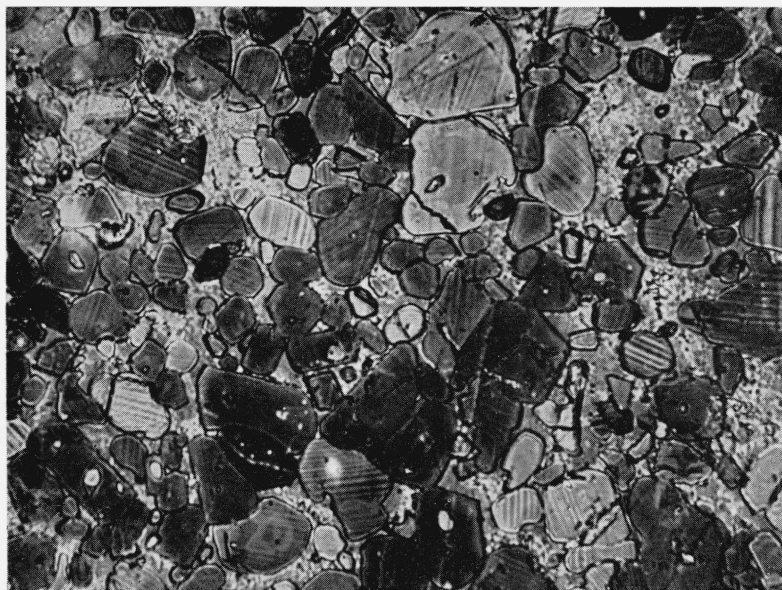


FIGURE 12.—*Same field as figure 11 after the same etching treatment and an additional etching with 10 percent KOH.*

The mottled character and the marked differentiation of the interstitial material are shown. Reflected light. Magnification, $\times 730$.

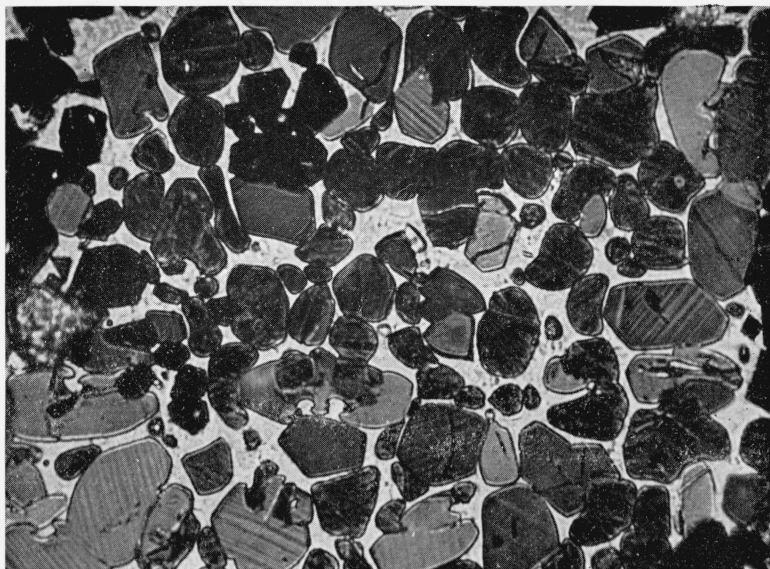


FIGURE 13.—*Laboratory-prepared low-heat clinker quenched after heating at 1,340° C. Etched with water and 1-percent alcoholic solution of HNO_3 . Shows greater differentiation of interstitial material than figure 11. Reflected light. Magnification, $\times 730$.*

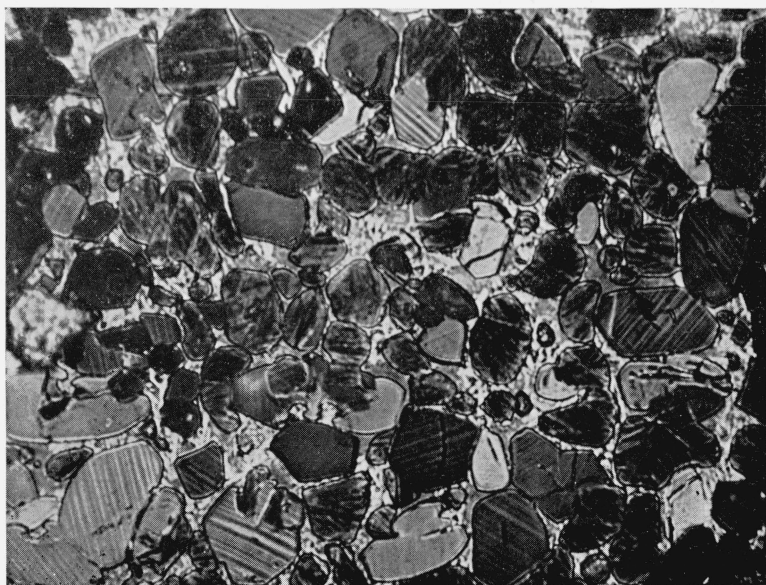


FIGURE 14.—*Same field as figure 13 after the same etching treatment and an additional etching with 10 percent KOH. The phase separation in the interstitial material is shown. Reflected light. Magnification, $\times 730$.*

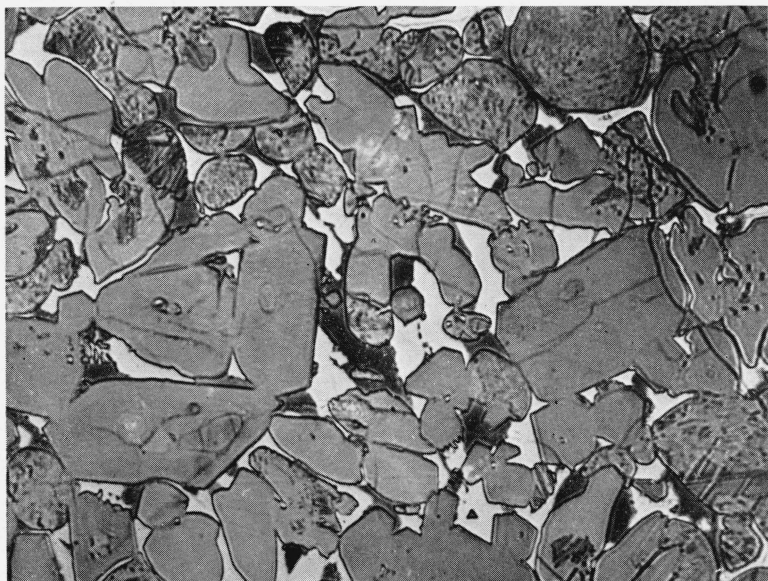


FIGURE 15.—*Laboratory-prepared low-heat clinker quenched after cooling from 1,350 to 1,330° C.*

Marked distinction between interstitial phases (C_4AF and C_3A) is shown. Magnification, $\times 730$.

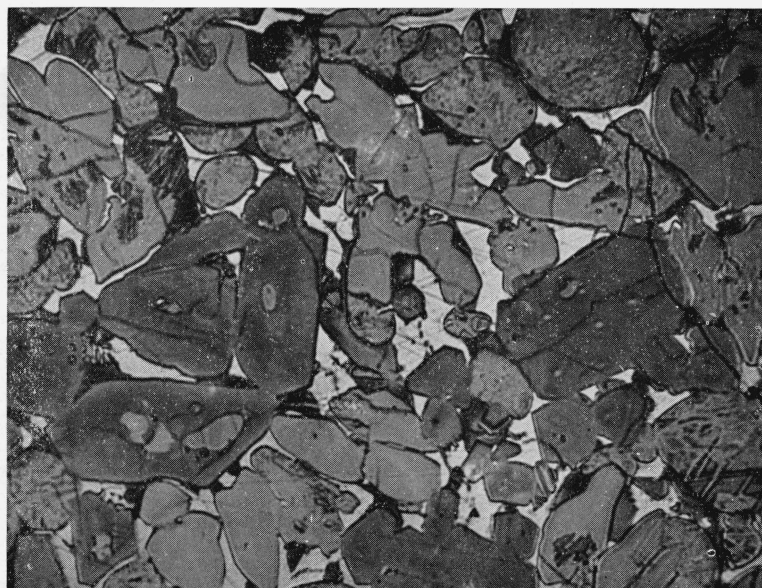


FIGURE 16.—*Same field as figure 15 after the same etching treatment and an additional etching with 10 percent KOH.*

No increase in distinction of interstitial phases over that in figure 15 is shown. Reflected light. Magnification, $\times 730$.

2. QUANTITATIVE ANALYSES

The amount of glass made visible by the KOH solution was so much greater than that revealed by the HNO_3 solution in certain clinker samples that it was decided to reanalyze quantitatively for $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ and glass all those samples whose analyses were reported in the previous paper [1]. The methods of mounting the clinker specimens and of measuring the phases were the same as described in that paper. The polished surfaces of the clinker fragments were etched first with distilled water for 3 seconds, then with an alcoholic solution of 0.25 percent HNO_3 for 3 seconds to provide satisfactory distinction between the silicates and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, and finally with a 10 percent aqueous solution of KOH at 29°C for 15 seconds.

TABLE 2.—Compositions of commercial clinker samples as determined by different methods

Clinker ¹	Free CaO plus free MgO ² (microscopic)	2CaO.SiO ₂ plus 3CaO.SiO ₂ (microscopic)	Light interstitial			Crystalline dark interstitial ²	Glass			Al ₂ O ₃ /Fe ₂ O ₃ ratio
			Calculated 4CaO.Al ₂ O ₃ .Fe ₂ O ₃ ³	First microscopic ²	Second microscopic		First microscopic ²	Second microscopic	Lerch method	
	Volume (%)	Volume (%)	Volume (%)	Volume (%)	Volume (%)	Volume (%)	Volume (%)	Volume (%)	Weight (%)	Volume (%)
1.....	3	79	13	16	13	1	1	4	3	0.86
2.....	0	76	16	22	15	0	2	9	5	.89
3.....	0	75	16	18	17	4	4	4	-----	.91
4.....	0	68	19	27	24	1	7	7	-----	.91
5.....	3	72	16	21	17	2	2	6	5	.92
6.....	2	78	14	17	14	1	2	5	7	.92
7.....	4	76	13	17	11	0	2	9	-----	1.01
8.....	2	79	10	16	10	1	2	8	-----	1.07
9.....	3	74	14	19	17	1	2	5	6	1.12
10.....	2	76	13	19	14	1	2	7	3	1.12
11.....	1	74	13	20	15	1	4	9	12	1.12
12.....	2	77	12	18	14	0	3	7	10	1.12
13.....	0	81	12	16	12	2	1	5	-----	1.22
14.....	1	74	14	21	21	1	3	-----	-----	1.23
15.....	1	72	13	22	19	1	4	7	-----	1.25
16.....	0	77	11	20	12	1	2	10	5	1.34
17.....	0	85	6	10	7	3	2	5	11	1.73
18.....	1	70	19	19	13	6	4	8	5	1.78
19.....	1	72	9	9	9	9	9	10	13	2.07
20.....	0	75	8	9	9	13	3	9	-----	2.11
21.....	1	71	8	6	8	12	10	8	-----	2.53
22.....	3	78	5	5	5	6	8	8	-----	2.64
23.....	2	69	8	9	9	14	6	6	-----	2.68
24.....	5	73	5	6	6	6	10	10	-----	2.78
25.....	3	75	6	4	6	8	10	8	13	2.89
26.....	0	76	5	5	6	15	4	3	-----	3.73

¹ Same designation as in Research Paper 1135, table 2.

² Determined by method described in Research Paper 1135.

³ Calculated by the Bogue method from the chemical composition.

The results of this analysis are given in table 2 under the headings, "Light interstitial—2d microscopic" and "Glass—2d microscopic." For comparison, these columns are set adjacent to columns with the subheadings "1st microscopic," under which are given the results for light interstitial material and glass as reported in Research Paper 1135. The table also gives the microscopically determined free CaO plus free MgO, $2\text{CaO} \cdot \text{SiO}_2$ plus $3\text{CaO} \cdot \text{SiO}_2$, the crystalline dark interstitial

material, $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ as calculated by the Bogue method, glass by the heat-of-solution method (designated the Lerch method), and the $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ ratio. Unlike table 2 of Research Paper 1135, all percentage values, except those for the Lerch method, are given here on the volume basis because no satisfactory density values can be assigned to the glasses to convert volume percentages as determined microscopically to weight percentages.

It is evident from an inspection of the table that the values for glass are higher and those for $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ are lower by the second microscopical method (using the KOH etch) than by the first microscopical method (using the HNO_3 etch) for all samples with $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ ratios less than 2.00. For ratios greater than 2.00, the values by the two methods are approximately the same. Consequently, the quantitative analyses provide additional evidence that the nitric acid solution etches glasses low in iron but fails to etch those high in iron, whereas the potassium hydroxide solution etches both.

Comparing the results for glass by the first and second microscopical methods with those obtained by heat-of-solution shows closer agreement between the second microscopical and heat-of-solution methods. Nevertheless, there are still discrepancies, notably for samples 2, 10, and 18. In part these discrepancies are the results of errors in the microscopical determination as, for example, the inability to distinguish and to measure accurately the amounts of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ and glass in areas where very fine particles of these two constituents are intimately mixed, and in part these discrepancies are the results of acknowledged errors [3] in the heat-of-solution method.

III. SUMMARY

A method of etching the polished surfaces of portland cement clinkers with KOH solution is described. This method permits the detection of glass containing considerable iron which has been hitherto overlooked in microscopical examination. The results of quantitative microscopical analysis using this technique are reported and compared with the results obtained by an older method.

The later results are practically identical with the earlier results for clinkers with $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ ratios greater than 2.00, but for those with ratios less than 2.00, the later results give more glass and less $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ than the earlier results. The quantitative results for glass by the later microscopical technique are more nearly in agreement with the results by an independent method involving the determination of heat-of-solution.

IV. REFERENCES

- [1] H. Insley, E. P. Flint, E. S. Newman, and J. A. Swenson, *J. Research NBS* **21**, 355 (1938) RP1135.
- [2] R. H. Bogue, *Ind. Eng. Chem., Anal. Ed.* **1**, 192 (1929).
- [3] Wm. Lerch and L. T. Brownmiller, *J. Research NBS* **18**, 609 (1937) RP997.
- [4] B. Tavasci, *Giorn. Chim. Ind. Applicata* **16**, 538 (1934).
- [5] F. M. Lea and T. W. Parker, *Bldg. Research Tech. Paper No. 16*, Dept. Sci. Ind. Research (England) (1935).
- [6] T. W. Parker and R. W. Nurse, *J. Soc. Chem. Ind.* **58**, 255 (1939).

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